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AGE-HARDENING COPPER-BASE ALLOY AND PROCESSING

Cross-Reference to Related Patent Application

This patent application claims priority to United States Provisional Patent Application, Serial No. 60/410,592, entitled "Age-Hardening Copper-Base Alloy and Processing," that was filed on September 13, 2002. The subject matter of that provisional patent application is incorporated by reference in its entirety herein.

Background of the Invention

1. Field of the Invention

This invention relates to an age-hardening copper-base alloy and a processing method to make commercially useful products from that alloy. More particularly, a copper alloy containing from 0.35% to 5%, by weight, titanium is wrought to finish gauge by a process that includes an in-process solution anneal and at least one age anneal. The resultant product has an electrical conductivity in excess of 50% IACS and a yield strength in excess of 105 ksi.

2. Description of Related Art

Throughout this patent application, all compositions are in weight percent and all mechanical and electrical testing was performed at room temperature (nominally 22°C), unless otherwise specified. The word "about" implies ±10% and the word "base" as in copper-base, means the alloy contains at least 50%, by weight, of the specified base element. The terms "rolling" or "rolled" are intended to encompass drawing or drawn or any other form of cold reduction, for example, as used in the manufacture and processing of wire, rod or tubing.

Many different types of electrical connectors are formed from copper-base alloys. Properties important for an electrical connector include yield strength, bend formability, resistance to stress relaxation, modulus of elasticity, ultimate tensile strength and electrical conductivity.

Target values for these properties and the relative importance of the properties are dependent on the intended application of products manufactured from the subject copper alloys. The following property descriptions are generic for many intended applications, but the target values are specific for under the hood automotive applications.

The yield strength is the stress at which a material exhibits a specified deviation, typically an offset of 0.2%, from proportionality of stress and strain. This is indicative of the stress at which plastic deformation becomes dominant with respect to elastic deformation. It is desirable for copper alloys utilized as connectors to have a yield strength of at least 105 ksi, that is at least approximately 724 MPa.

Stress relaxation becomes apparent when an external stress is applied to a metallic strip in service, such as when the strip is loaded after having been bent into a connector. The metal reacts by developing an equal and opposite internal stress. If the metal is held in a strained position, the internal stress will decrease as a function of both time and temperature. This phenomenon occurs because of the conversion of elastic strain in the metal to plastic, or permanent strain, by microplastic flow.

Copper based electrical connectors must maintain above a threshold contact force on a mating member for prolonged times for good electrical connection. Stress relaxation reduces the contact force to below the threshold leading to an open circuit. It is desirable for a copper alloy for connector applications to maintain at least 95% of the initial stress when exposed to a temperature of 105°C for 1000 hours and to maintain at least 85% of the initial stress when exposed to a temperature of 150°C for 1000 hours.

The modulus of elasticity, also known as Young's modulus, is a measure of the rigidity or stiffness of a metal and is the ratio of stress to corresponding strain in the elastic region. Since the modulus of elasticity is a measure of the stiffness of a material, a high modulus, on the order of 140 Gpa ($20x10^3$ ksi) is desirable.

Bendability determines the minimum bend radius (MBR) which identifies how severe a bend may be formed in a metallic strip without fracture along the outside radius of the bend. The MBR is an important property for connectors where different shapes are to be formed with bends at various angles.

Bend formability may be expressed as, MBR/t, where t is the thickness of the metal strip. MBR/t is a ratio of the minimum radius of curvature of a mandrel about which the metallic strip can be bent without failure to the thickness of the strip. The "mandrel" test is specified in ASTM (American Society for Testing and Materials) designation E290-92, entitled Standard Test Method for Semi-Guided Bend Test for Ductility of Metallic Materials, and is incorporated by reference in its entirety herein.

It is desirable for the MBR/t to be substantially isotropic, a similar value in the "good way", bend axis perpendicular to the rolling direction of the metallic strip, as well as the "bad way", bend axis parallel to the rolling direction of the metallic strip. It is desirable for the MBR/t to be about 1.5 or less for a 90° bend and about 2 or less for a 180° bend.

Alternatively, the bend formability for a 90° bend may be evaluated utilizing a block having a V-shaped recess and a punch with a working surface having a desired radius. In the "V-block" method, a strip of the copper alloy in the temper to be tested is disposed between the block and the punch and when the punch is driven down into the recess, the desired bend is formed in the strip.

Related to the V-block method is the 180° "form punch" method in which a punch with a cylindrical working surface is used to shape a strip of copper alloy into a 180° bend.

Both the V-block method and the form punch method are specified in ASTM designation B820-98, entitled Standard Test Method for Bend Test for Formability of Copper Alloy Spring Material, that is incorporated by reference in its entirety herein.

For a given metal sample, both methods give quantifiable bendability results and either method may be utilized to determine relative bendability.

The ultimate tensile strength is a ratio of the maximum load a strip withstands before failure during a tensile test divided by the initial cross-sectional area of the strip. It is desirable for the ultimate tensile strength to be about 110 ksi, that is approximately 760 MPa.

Electrical conductivity is expressed in % IACS (International Annealed Copper Standard) in which unalloyed copper is defined as having an electrical conductivity of 100% IACS at 20°C.

Copper-base alloys containing titanium are disclosed in United States patent numbers 4,601,879 and 4,612,167, among others. The 4,601,879 patent discloses a copper-base alloy containing 0.25% to 3.0% of nickel, 0.25% to 3.0% of tin and 0.12% to 1.5% of titanium. Exemplary alloys have an electrical conductivity of between 48.5% and 51.4% IACS and a yield strength of between 82.5 ksi and 84 ksi.

The 4,612,167 patent discloses a copper alloy containing 0.8% to 4.0% of nickel and 0.2% to 4.0% of titanium. Exemplary alloys have an electrical conductivity of 51% IACS and a yield strength of 96.2 ksi to 98.5 ksi. Both the 4,601,879 patent and the 4,612,167 patent are incorporated by reference in their entireties herein.

AMAX Copper, Inc. (Greenwich, CT) has commercialized copper-nickel-titanium alloys having nominal compositions of Cu-2%Ni-1%Ti and Cu-5%Ni-2.5%Ti. The reported properties for the Cu-2%Ni-1%Ti alloy are yield strength 64 - 80 ksi; ultimate tensile strength 73 - 95 ksi; elongation 9%; and electrical conductivity 50 - 60% IACS. The reported properties for the Cu-5%Ni-2.5%Ti alloy are yield strength 90 - 100 ksi;

ultimate tensile strength 108 ksi UTS; elongation 10 %; and electrical conductivity 40 - 53% IACS.

Many current and future applications for these copper alloys will require an electrical conductivity of at least 50% IACS and a yield strength of at least 105 ksi. There remains a need for copper-titanium alloys and processes for manufacturing the copper-titanium alloys capable of achieving the required levels of electrical conductivity and strength.

Summary Of The Invention

In accordance with the invention, there is provided an age-hardening copper-base alloy and methods to process this alloy to form a commercially useful product for any application requiring high yield strength and moderately high electrical conductivity. Typical forms for the product include strip, plate, wire, foil, tube, powder or cast form. The alloys when processed according to the methods of the invention achieve a yield strength of at least 105 ksi and an electrical conductivity of 50% IACS making the alloys particularly suited for use in electrical connectors and interconnections.

The alloys consisting essentially of, by weight, from 0.35% to 5% titanium, from 0.001% to 10% of X, where X is selected from Ni, Fe, Sn, P, Al, Zn, Si, Pb, Be, Mn, Mg, Bi, S, Te, Se, Ag, As, Sb, Zr, B, Cr and Co and combinations thereof and the balance is copper and inevitable impurities. The alloy has an electrical conductivity of at least 50% IACS and a yield strength of at least 105 ksi..

In a preferred aspect of the invention, the alloy consists essentially of from 0.35% to 2.5% titanium, from 0.5% to 5.0% nickel, from 0.5% to 0.8% of iron, cobalt and mixtures thereof, from 0.01% to 1.0% magnesium, up to 1% of Cr, Zr, Ag and combinations thereof and the balance is copper and inevitable impurities.

These alloys, when beryllium is not present, avoid the potentially dangerous health issues associated with current beryllium-copper alloys, while offering similar combinations of strength and conductivity.

Brief Description of the Several Drawings

Figure 1 illustrates in flow chart format a first method for processing the copper alloys of the invention.

Figure 2 illustrates in flow chart format a second method for processing the copper alloys of the invention.

Figure 3 illustrates in flow chart format a third method for processing the copper alloys of the invention.

Detailed Description Of The Invention

Copper alloys having a combination of strength and electrical conductivity, as well as good formability and a resistance to stress relaxation are in demand for many electrical current carrying applications. Two exemplary applications are under-the-hood automotive applications and multimedia applications (such as computers, DVD players, CD readers and the like).

For automotive applications, there is a need for copper alloys with good formability, an electrical conductivity of at least 50% IACS and stress relaxation resistance up to 200°C. For multimedia interconnect applications, there is a need for copper alloys with a yield strength in excess of 105 ksi, an electrical conductivity in excess of 50% IACS and mechanical stability at room and slightly higher service temperatures, as characterized, by excellent stress relaxation resistance at about 100°C.

The alloy compositions when processed by the methods of this invention surprisingly provide an optimum combination of properties for meeting the needs for

both automotive and multimedia applications, as well as other electrical and electronic applications. The alloys can provide moderately high strength along with high conductivity and moderately high conductivity along with very high strength.

The alloys of the present invention have compositions containing Cu-Ti-X, where X is selected from Ni, Fe, Sn, P, Al, Zn, Si, Pb, Bi, S, Te, Se, Be, Mn, Mg, Ag, As, Sb, Zr, B, Cr and Co and combinations thereof. The titanium content is from 0.35% to 5% and the sum total of the "X" elements is from 0.001% to 10%.

Strength and electrical conductivity are maximized when X is selected from the group consisting of Ni, Fe, Co, Mg, Cr, Zr, Ag and mixtures thereof

Oxygen, sulfur and carbon may be present in the alloys of the invention in amounts typically found in either electrolytic (cathode) copper or remelted copper or copper alloy scrap. Typically, the amount of each of these elements will be in the range of from about 2 ppm to about 50 ppm and preferably, each is present in an amount of less than 20 ppm.

Other additions that influence the properties of the alloy may also be included. Such additions include those that improve the free machinability of the alloy, such as bismuth, lead, tellurium, sulfur and selenium. When added to enhance free machinability, these additions may be present in an amount of up to 2%. Preferably, the total of free machinability additions is between about 0.8% and 1.5%.

Typical impurities found in copper alloys, particularly in copper alloys formed from recycled or scrap copper, may be present in an amount of up to about 1%, in total. As a non-exclusive list, such impurities include magnesium, aluminum, silver, silicon, cadmium, bismuth, manganese, cobalt, germanium, arsenic, gold, platinum, palladium, hafnium, zirconium, indium, antimony, chromium, vanadium, and beryllium. Each impurity should be present in an amount of less than 0.35%, and preferably in an amount of less than 0.1%.

It should be recognized that some of the above-recited impurities, or others, in amounts overlapping the above specified impurity ranges, may have a beneficial effect on the copper alloys of the invention. For example, strength or stampability may be improved. This invention is intended to encompass such low level additions.

In a more preferred embodiment of the invention, the titanium content is from 0.35% to 2.5% and in a most preferred embodiment, the titanium content is from 0.8% to 1.4%

When the titanium is in solution in the copper alloy matrix, electrical conductivity is severely degraded. Therefore, "X" should preferably be effective to cause titanium to precipitate from solution during an age anneal. Suitable elements for "X" to enhance such precipitation include Ni, Fe, Sn, P, Al, Si, S, Mg, Cr, Co and combinations of these elements.

One preferred addition is nickel. A combination of Ni and Ti provides precipitates of CuNiTi and the presence of Fe and Ti provides precipitates of Fe_2Ti.

Another preferred addition is magnesium. An addition of Mg increases stress relaxation resistance and softening resistance in finished gauge and temper products. The Mg also provides softening resistance during in-process aging annealing heat treatments.

When present at low levels, additions of Cr, Zr and/or Ag provide increased strengthening without unduly reducing conductivity.

One preferred alloy in accordance with the invention that has an improved combination of yield strength, electrical conductivity, stress relaxation resistance, along with modest levels of bendability consists essentially of

about 0.5 - 5.0% Nickel
about 0.35 - 2.5% Titanium
about 0.5 - 0.8% Iron or Cobalt
about 0.01 - 1.0% Magnesium,

with optionally up to about 1.0% of one or more of Sn, P, Al, Zn, Si, Pb, Bi, S, Te, Se, Be, Mn, Mg, Ag, As, Sb, Zr, B, Cr and mixtures thereof,

and the balance copper and impurities.

Preferably the optional elements comprise up to 1% of one or more of Cr, Zr and Ag.

More preferred ranges for this alloy are:

about 0.8 - 1.7% Nickel

about 0.8 - 1.4% Titanium

about 0.90 - 1.10% Iron, or Cobalt

about 0.10 - 0.40% Magnesium,

with up to about 1.0% of one or more of Cr, Zr, Ag or Sn and mixtures thereof,

and the balance Copper and impurities

In a first embodiment of the invention, the alloy composition and processing provide a yield strength of at least about 115 ksi and preferably a yield strength of at least about 120 ksi. For this embodiment, the conductivity is up to about 40% IACS. In a second embodiment of the invention, the composition and processing provide a yield strength of more than about 105 ksi, and preferably up to about 115 ksi. In this second embodiment, the electrical conductivity of the alloy is preferably from about 45% to about 55% IACS. In a third embodiment, the composition and processing provide a yield strength of from about 80 ksi to about 100 ksi and the electrical conductivity is between about 55% and about 65% IACS.

Fig. 1 illustrates in flow chart format, a process in accordance with a first embodiment of the invention. The alloy of the invention is melted and cast 10 in accordance with conventional practice. The cast alloy is hot rolled 12 at from about 750°C to about 1,000°C. After milling to remove oxide, the alloy is then cold rolled 14 to

a reduction in cross-sectional area transverse to the rolling direction ("reduction in area") of from about 50% to about 99%. The alloy may then be solutionized 16 at a solution annealing temperature of from about 850 to about 1,000°C for from about 10 seconds to about one hour, followed by a quench 18 or rapid cool to ambient temperature to obtain equiaxed grains with an average grain size of about 5 and 20 μm. Thereafter the alloy may be first cold rolled 20 up to about 80% reduction in area, preferably about 30% to about 80% reduction in area. The first cold roll 20 is followed by a first anneal 22 at a temperature of from about 400°C to about 650°C and preferably from about 450 °C to about 600°C for from about 1 minute to about 10 hours and preferably from about 1 to about 8 hours. The alloy is then second cold rolled 24 from about a 10% to about a 50% reduction in area to finished gauge. The second cold roll may be followed by a second anneal 26 at about 150°C to about 600°C and preferably from about 200°C to about 500°C for from about 15 seconds to about 10 hours.

Alternatively in accordance with another embodiment, the alloy is processed to finished gauge without using an in-process solutionizing heat treatment. That is, it can be processed to finish using cycles of lower temperature annealing treatments and intervening cold work. This alternative process is especially useful for making a product with higher electrical conductivity levels.

Fig. 2 illustrates in flow chart representation an alternative process of the invention. The alloy of the invention is melted and cast 10 in accordance with conventional practice. The cast alloy is hot rolled 12 at from about 750°C to about 1,000°C. and then quenched or quickly cooled. After milling to remove oxide, the hot rolled alloy is then cold rolled 14 to a reduction in area of from about 50% to about 99%. The alloy may then be first annealed 28 at an annealing temperature of from about 400°C to about 650°C for from about 15 secs. to about 10 hours. The cold rolling and first annealing steps may optionally be repeated, if desired The alloy is then cold rolled 30 from about 40% to about 80% reduction in area followed by a second anneal 32 at

from about 400°C to about 650°C and preferably from about 450°C to about 600°C for from about 1 to about 10 hours. The alloy is then cold rolled 34 from about a 10% to about a 50% reduction in area to finished gauge. This may optionally be followed by a third anneal 26 at about 150°C to about 600°C and preferably from about 200°C to about 500°C for from about 15 seconds to about 10 hours.

A second alternative preferred embodiment of the process of this invention employs an alloy in the preferred composition ranges. This process is capable of making the alloy of this invention with nominal properties of about 110 ksi YS and about 50% IACS conductivity. With reference to Fig. 3, the alloy is melted and cast 10 in accordance with conventional practice. The cast alloy is hot rolled 12 at from about 750°C to about 1,000°C. After milling to remove oxide the hot rolled alloy is then cold rolled 14 to a reduction in area of from about 50% to about 99%. The alloy is then solutionized 16 at a temperature of from about 950°C to about 1,000°C for from about 15 seconds to about 1 hour. The alloy is next cold rolled 20 to from about a 40% to about a 60% reduction in area and then first annealed 28 at about 400°C to about 650°C and preferably 450°C to about 600°C for from about 1 to about 10 hours and preferably from about 1 to about 3 hours. The first anneal 28 is followed by cold rolling 30 from about a 40% to about a 60% reduction in area. The alloy is then second annealed 32 at a lower temperature than the first anneal 28. The second anneal is at a temperature of from about 375°C to about 550°C for from about 1 to about 3 hrs. The doubly annealed alloy is then cold rolled 34 at least about 30% reduction in area to a finished gauge where it may be annealed a third time 26 at a temperature of from about 150°C to about 600°C and preferably from about 200°C to about 500°C for from about 1 to about 3 hours.

The alloys of the invention and the processes of the invention are better understood with reference to the Examples that follow.

Examples

In the examples that follow some of the process descriptions, properties and units are written in an abbreviated form. For example, " = inches, WQ = water quench, a slash mark / = for, SA = solution anneal, CR = cold rolled or cold reduced, YS = yield strength, TS = tensile strength, EL = elongation, %IACS = electrical conductivity, MBR/t = minimum bend radius divided by the strip thickness, SR = stress relaxation resistance, Gs = grain size, μm = microns or micrometers, beg. = begin, recr. = recrystallized, n.c.r. = not completely recrystallized, sec. or s = seconds, hrs. or h = hours, MS/m = mega-siemens per meter and ksi =thousands of pounds per square inch.

Example 1

Utilizing the process illustrated in Fig. 1, a series of ten pound laboratory ingots with the analyzed compositions listed in Table 1 were melted in a silica crucible and Durville cast into steel molds. After gating the ingots were 4"X4"X1.75". After soaking for three hours at 950°C, the ingots were hot rolled in three passes to 1.1", reheated at 950°C for ten minutes, and further hot rolled in three passes to 0.50", followed by a water quench. The resultant hot rolled plates were homogenized by soaking for two hours at 1,000°C followed by a water quench. After trimming and milling to remove oxide coating, the alloys were cold rolled to 0.050". The alloys were then solutionized at a temperature of 1000°C for from 20 to 60 seconds, with the exception of alloy J346 which was solutionized at 950°C for 60 seconds. Following solutionization and quenching, the alloys were cold rolled 50% to 0.025" and age annealed at 550°C for 3 hours The alloys were then cold rolled 50% to 0.0125" gauge and relief annealed at 275°C for 2 hours and the properties reported in Table 2 measured.

The data in Table 2 show that high values of yield strength, from 90 ksi to 111 ksi, and electrical conductivity, from 38.2% IACS to 63.8% IACS were obtained. The stress relaxation resistance obtained was close to the desired value of 95% after 1000

hours at 105°C for the Cu-Ni-Ti-Fe alloys J345 and J346. The desired value was achieved by the Cu-Ni-Ti-Mg alloy J354.

Table 1 - Alloys of Example 1

Alloy Identification Number (ID)	Analyzed composition, wt%
J345	Cu - 2.32 Ni - 1.96 Ti - 1.06 Fe
J346	Cu - 1.16 Ni - 1.32 Ti - 0.92 Fe
J347	Cu - 0.80 Ni - 0.80 Ti
J348	Cu - 0.89 Ni - 1.82 Ti - 1.04 Fe
J351	Cu - 2.45 Ni - 1.16 Ti
J354	Cu - 2.43 Ni - 1.18 Ti - 0.38 Mg

Table 2

Properties for the Relief Annealed Condition for Alloys Listed in Table 1

Alloy ID	Cond %IACS	YS/TS/El	90°-MBR/t good way / bad way	% SR 105°C 1,000 h	%SR 105°C 3,000 h
J345	42.9	106/ 122/ 2	2.7 / 8.8	90.4	89.5
J346	56.1	97 / 102/ 3	1.4 / 2.9	88.2	87.3
J347	34.6	106/ 117/ 1	2.7 / 8.8	--	--
J348	38.2	111/ 124 / 4	1.9 / 7.5	--	--
J351	63.8	90 / 93 / 1	1.4 / 2.2	--	--
J354	47.0	109/ 115/ 2	5.0 / 8.8	95.1	93.9

Example 2

In accordance with the process illustrated in Fig. 2, the alloys of Table 1 were processed as in Example 1 up through the homogenization heat treatment at hot rolled plate gauge. In this example, the alloys were processed to finish gauge without an in-process solutionizing heat treatment. After trimming and milling to remove the oxide coating, the alloys were cold rolled to 0.100" and given a first aging anneal at 550°C for 3 hours. The alloys were then cold rolled 70% to 0.030" and subjected to a second aging anneal at 525°C for 3 hours. The alloys were then cold rolled 50% to 0.015" gauge and relief annealed 275°C for 2 hrs in which condition the properties recited in Table 3 were measured.

Consistent with the data in Table 2, the alloys of this example had a combination of a high yield strength, from 98 ksi to 107 ksi, but with higher electrical conductivity of between 49.9% IACS and 69.7% IACS. Enhanced stress relaxation resistance is obtained when either Fe or Mg is added to the base Cu-Ni-Ti alloy. The data in Table 3 show that the highest stress relaxation resistance obtained with a Mg addition to a Cu-Ni-Ti alloy; compare alloy J354 to alloy J351.

Table 3 Properties for the Relief Annealed Condition for Alloys Listed in Table 1					
Alloy ID	**Cond. %IACS**	**YS/TS/El**	**90°-MBR/t**	**% SR 105°C 1,000 h**	**%SR 105°C 3,000 h**
J345	57.8	107/ 115/ 4	3.1 / 4.2	86.9	85.9
J346	63.2	98 / 104/ 5	0.8 / 4.2	85.8	84.7
J347	49.9	105/ 111/ 3	0.8 / 5.2	--	--
J348	58.8	104/ 112/ 6	2.1 / 5.2	--	--
J351	69.7	98 / 104/ 4	0.8 / 0.8	82.7	80.8
J354	60.8	101/ 108/ 5	2.4 / 4.2	92.4	90.4

Example 3

In accordance with the process illustrated in Fig. 1, a series of ten pound laboratory ingots with the analyzed compositions listed in Table 4 were melted in silica crucibles and Durville cast into steel molds. After gating the ingots were 4"X4"X1.75". After soaking three hours at 950°C they were hot rolled in three passes to 1.1" thick, reheated at 950°C / ten minutes, and further hot rolled in three passes to 0.50" thick, followed by a water quench. After trimming and milling to remove the oxide coating, the alloys were cold rolled to 0.050".

The alloys other than J477 were then solution heat treated at 1,000°C for 25 seconds followed by a water quench to yield a controlled, fine, recrystallized grain size in the range 12 - 24 μm in diameter. Alloy J477 was solution heat treated at 950°C / 25 secs + WQ, yielding a grain size of 9 μm.

All alloys were then cold rolled 50% to 0.025" thick and subjected to an aging anneal at 550°C for a time effective to maximize electrical conductivity without unduly

softening the matrix. The times at 550°C are reported in Table 5. The alloys were then cold rolled 50% to 0.0125" gauge and relief annealed at 275°C for 2 hrs at which condition the properties in Table 5 were measured.

The data in Table 5 show that, while the base alloy J477 offers a good combination of properties (92 ksi YS and 58.1% IACS conductivity), the Fe addition increases the strength of the base alloy (J483 versus J477) to 100 ksi with only a slight reduction in electrical conductivity. Moreover, the advantage of the Mg addition, while maintaining consistent amounts of Ni, Ti and Fe, for increasing stress relaxation resistance at 105°C is shown by comparing alloy J491 to J481. The advantage of Mg is also shown by comparison of the properties of alloy J491 (Table 5) compared to those of J345 and J346 in Table 2.

Table 4

Alloys of Example 3

Alloy Identification No.	Analyzed composition, wt%
J477	Cu - 1.41 Ni – 0.71 Ti
J481	Cu - 1.00 Ni - 0.98 Ti - 0.99 Fe
J483	Cu - 1.42 Ni - 0.87 Ti - 0.53 Fe
J485	Cu - 0.97 Ni - 1.40 Ti - 1.01 Fe
J486	Cu - 1.86 Ni - 1.43 Ti - 0.98 Fe
J491	Cu - 0.98 Ni - 0.94 Ti - 1.00 Fe - 0.35 Mg

Table 5 Properties in the relief annealed condition for alloys listed in Table 4						
Alloy ID	**550°C/No. hrs**	**Cond. %IACS**	**YS/TS/EI**	**90°-MBR/t**	**% SR 1,000 hrs. 105°C**	**%SR 1,000 hrs. 150°C**
J477	3	58.1	92 / 96 / 1	1.1 / 1.8		
J481	5	56.6	96 / 100 / 4	1.1 / 1.8	92	90
J483	8	54.0	100 / 104 / 3	1.8 / 2.2	93	86
J485	8	53.6	101 / 106 / 5	0.8 / 2.1		
J486	8	52.8	102 / 106 / 1			
J491	8	55.0	98 / 102 / 5	1.4 / 2.4	96	86

Example 4

IN accordance with the process illustrated in Fig. 2, the alloys of Table 4 were processed to finish gauge without using an in-process solutionizing heat treatment. After trimming and milling to remove the oxide coating, the alloys in the as hot rolled condition were cold rolled to 0.050" gauge and given a first aging anneal at a temperature and time as shown in Table 6 effective to maximize electrical conductivity. The alloys were then cold rolled 50% to 0.025" gauge and subjected to a second aging anneal at a temperature and time as shown in Table 6 selected to maximize the conductivity without unduly softening the matrix. The specific aging anneals applied to each alloy are noted in Table 6. The alloys were then cold rolled 50% to 0.0125" gauge and relief annealed at 275°C for 2 hrs. at which condition the properties in Table 7 were measured. Using this process, the alloys with Fe and Mg additions provide lower, but still good, strength with higher electrical conductivity and good stress relaxation resistance.

Table 6 Aging anneals applied to the alloys in Example 4			
Alloy Identity	Aging treatment at 0.050" gauge	Aging treatment at 0.025" gauge	YS, ksi / Conductivity % IACS
J477	525°C / 2 hrs	450°C / 1 hr	76 / 69.4%
J481	550°C / 2 hrs	500°C / 1 hr	62 / 69.4%
J483	550°C / 2 hrs	500°C / 1 hr	80 / 65.1%
J485	550°C / 4 hrs	500°C / 1 hr	80 / 65.2%
J486	550°C / 2 hrs	450°C / 1 hr	70 / 66.6%
J491	550°C / 4 hrs	500°C / 1 hr	65 / 61.0%

Table 7 Properties for the relief annealed condition for alloys listed in Table 4					
	CR 0.0125" + relief annealed 275°C / 2 hrs				
Alloy ID	Cond %IACS	YS/TS/El	90°-MBR/t	% SR 105°C 1,000 hrs.	%SR 150°C 1,000 hrs.
J477	64.1	84 / 91 / 3	1.8 / 3.8		
J481	68.1	79 / 88 / 4	1.7 / 1.9	82	76
J483	62.5	88 / 94 / 4	1.8 / 2.2	86	82
J485	61.3	93 / 102 / 5	1.8 / 3.8		
J486	64.8	83 / 92 / 5			
J491	60.3	89 / 94 / 5	1.9 / 2.2	94	77

Example 5

In accordance with the process illustrated in Fig. 3, a series of ten pound laboratory ingots with the analyzed compositions listed in Table 8 were melted in silica crucibles and Durville cast into steel molds After gating the ingots were 4"X4"X1.75". After soaking three hours at 950°C they were hot rolled in three passes to 1.1" thick,

reheated at 950°C for ten minutes, and further hot rolled in three passes to 0.50" gauge, followed by a water quench. After trimming and milling to remove the oxide coating, the alloys were cold rolled to 0.100" thick and solution heat treated in a furnace at 950°C for 40 seconds followed by a water quench to yield a controlled, fine, recrystallized grain size in the range 8.0 - 12 μm. They were then cold rolled 50% to 0.050" gauge and subjected to an aging anneal at 565°C for 3 hrs, designed to maximize the conductivity without unduly softening the matrix. The alloys were then cold rolled 50% to 0.025" gauge and given a second aging anneal of 410°C for 2 hrs, cold rolled to 0.010". This was followed by a relief anneal of 250°C for 2 hrs for which condition the properties in Table 9 were measured.

Table 8

Alloys of Example 5

Alloy Identification Number	Analyzed composition, wt%
J694	Cu - 1.78 Ni - 1.34 Ti - 0.98 Fe - 0.24 Mg
J698	Cu - 1.72 Ni - 1.42 Ti - 1.02 Fe - 0.24 Mg - 0.06 Zr
J699	Cu - 1.72 Ni - 1.35 Ti - 1.01 Fe - 0.23 Mg - 0.60 Ag
J700	Cu - 1.75 Ni - 1.37 Ti - 1.01 Fe - 0.23 Mg - 0.53 Cr

Table 9 Properties for the relief annealed condition for alloys listed in Table 8						
			410°C/2 h, 0.025"	CR 0.010" + 250°C / 2 hrs		
Alloy ID	**Ni / Ti**	**(Ni+Fe)/Ti**	**YS, ksi**	**Cond %IACS**	**YS/TS/El**	**90°-MBR/t**
J694	1.3	2.1	94	50.9	108 / 116 / 3	2.2 / 9.4
J698	0.8	1.9	93	51.3	111 / 119 / 3	2.6 / 7.8
J699	1.3	2.0	90	51.9	112 / 119 / 2	2.8 / 10.9
J700	1.3	2.0	93	49.5	110 / 118 / 2	2.6 / 6.2

Comparing baseline alloy J694 to zirconium containing alloy J698 demonstrates that a small amount of zirconium increases the yield strength without affecting electrical conductivity. A comparison of alloy J694 with silver containing alloy J699 demonstrates that a small amount of silver increases both the yield strength and the electrical conductivity. A comparison of alloy J694 with chromium containing alloy J700 demonstrates that an addition of a small amount of chromium increases the yield strength slightly with a slight penalty in electrical conductivity.

Example 6

In accordance with the process illustrated in Fig. 3, a series of ten pound laboratory ingots with the analyzed compositions listed in Table 10 were melted in silica crucibles and Durville cast into steel molds. After gating the ingots were 4"X4"X1.75". After soaking three hours at 950°C they were hot rolled in three passes to 1.1" thick, reheated at 950°C for ten minutes, and further hot rolled in three passes to 0.50" thick, followed by a water quench. After trimming and milling to remove the oxide coating, the alloys were cold rolled to 0.100" gauge and solution heat treated in a furnace at 1,000°C for 25-35 seconds followed by a water quench to yield a controlled, fine,

recrystallized grain size in the range 6 - 12 μm. They were then cold rolled 50% to 0.050" gauge and subjected to an aging anneal at 550 - 600°C for 3 - 4 hrs. The alloys were then cold rolled 50% to 0.025" gauge and again given an aging anneal 410 - 425°C for 2 hrs, followed by cold rolling to 0.010" and relief annealing at 250 - 275°C for 2 hrs.

The properties at finished gauge, listed in Table 11, show a better yield strength and conductivity combination was obtained with either a Mg addition (J604 compared to J603) and/or a Zr addition (J644 compared to J603).

Without the Mg addition, a Cr addition is not as effective by itself (Compare the low strengths of J646 in Table 11 (column D) with the higher strengths of J700 in Table 9). Note also from Table 11 how the Mg addition increases the yield strength (and tensile strength) values over the Mg range: 0, 0.16, 0.25, 0.31 wt% Mg addition to: 102 (110), 103 (112), 108 (116), 110 (118) ksi, respectively, at nearly constant conductivity values of about 48% IACS.

Table 10
Alloys of Example 6

Alloy Identification Number	Analyzed composition, wt%
J603	Cu - 1.86 Ni - 1.47Ti - 0.99 Fe
J604	Cu - 1.89 Ni - 1.33 Ti - 0.98 Fe - 0.25 Mg
J642	Cu - 1.61 Ni - 1.42 Ti - 1.04 Fe 0.16 Mg
J643	Cu - 1.61 Ni - 1.40 Ti - 1.02 Fe - 0.31 Mg
J644	Cu - 1.53 Ni - 1.37 Ti - 0.91 Fe - 0.19 Zr
J646	Cu - 1.61 Ni - 1.43 Ti - 0.98 Fe - 0.52 Cr

Table 11 Properties for the relief annealed condition at 0.010" gauge for alloys listed in Table 10						
	YS, ksi / UTS, ksi / Elong., % Conductivity, % IACS					
Process: Alloy ID	A	B	C	D	E	F
J603	88 / 97 / 4 62.4	91 / 100 / 4 56.0	101 / 110 / 4 53.4	102 / 110 / 3 48.1	103 / 112 / 3 50.3	103 / 111 / 3 46.9
J604	101 / 108 / 5 54.2	101 / 110 / 4 50.0	110 / 118 / 3 49.9	108 / 116 / 3 48.2	114 / 122 / 2 46.6	114 / 120 / 2 43.9
J642	93 / 101 / 3 60.1	94 / 104 / 4 56.0	105 / 112 / 3 53.9	103 / 112 / 3 51.3	106 / 114 / 3 53.8	106 / 113 / 3 50.6
J643	96 / 103 / 5 56.7	96 / 107 / 4 52.6	107 / 115 / 4 51.7	110 / 118 / 3 47.7	109 / 116 / 3 50.7	110 / 118 / 3 46.9
J644	87 / 98 / 4 64.7	97 / 107 / 4 61.1	105 / 114 / 3 56.8	107 / 116 / 4 50.3	108 / 117 / 3 53.4	108 / 116 / 3 47.6
J646	76 / 84 / 4 64.7	76 / 86 / 5 61.3	88 / 96 / 2 60.8	87 / 96 / 3 56.2	88 / 98 / 4 61.6	90 / 100 / 4 58.7

Example 7

This example illustrates how the composition and processing influences yield strength and electrical conductivity. Alloys J694 and J709 having the compositions recited in Table 12 were processed from 4"x4"x1.75" ingots by soaking for 3 hours at 950°C and hot rolling to 0.50 inch followed by a water quench. After trimming and milling to remove oxides, the alloya were cold rolled to 0.10 inch and solution heat treated at 1000°C for 35 seconds and water quenched. The alloys were then cold rolled to 0.05 inch, solutionized at 950°c for 35 seconds and water quenched. Further processing is as in Table 13 with properties recited in Table 14.

Table 12

Alloy	Composition
J694	Cu – 1.78 Ni – 1.34 Ti – 0.98 Fe – 0.24 Mg
J709	Cu – 0.93 Ni – 0.90 Ti – 1.05 Fe – 0.24 Mg

Table 13

Process	Process steps from 0.05 inch
J1	Anneal at 565°C for 3 hours + cold roll to 0.025 inch + anneal at 410°C for 2 hours + cold roll to 0.015 inch + anneal at 250°C for 2 hours
J2	Anneal at 565°C for 3 hours + cold roll to 0.025 inch + anneal at 410°C for 2 hours + cold roll to 0.008 inch + anneal at 250°C for 2 hours

Process	Alloy J694				Alloy J709			
	YS (ksi)	TS (ksi)	Elong (%)	Cond (%IACS)	YS (ksi)	TS (ksi)	Elong (%)	Cond (%IACS)
J1	117	122	1	42.8	111	115	1	42.8
J2	120	123	1	36.8	115	119	1	37.5

One or more embodiments of the present invention have been describe above. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.